
DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacturing method of the X type non-metal phthalocyanines which were excellent in the characteristic at the time of using it, for example for application members, such as an electro photography photo conductor, and were excellent in the long term storage stability of the various coating liquid for application member manufacture in more detail about the manufacturing method of X type non-metal phthalocyanines.

[0002] The X type non-metal phthalocyanines which cover a near-infrared region from a light region, and show high photosensitivity, It can use effectively as a photoactive substance in the optoelectric transducer using a photoelectric conversion operation of a substance, for example, a solar cell, a photosensor, an optical switching element, an electro photography photo conductor, etc., and is inquiring briskly as photosensitive paints for electro photography photo conductors especially in recent years.

[0003]

[Description of the Prior Art] In the various optoelectric-transducer division electro photography photo conductors which use a photoelectric conversion substance, although mineral matter, such as Se, Se/Te, Se/As, CdS, Si, and ZnO, was used conventionally, There is nothing that may fully be satisfied in respect of the size of a sensitization wavelength band, safety, processability, economical efficiency, etc., The organic compound of the various chemical structure which continues till recent years and is called an organic optical semiconductor (OPC and abbreviation) compensates the fault of mineral matter, it turns out that it is more than outstanding material, many useful OPC(s) are found out, and there are also some things already put in practical use.

[0004] Also in them, phthalocyanines are among the most outstanding OPC(s), and it is famous for having the feature excellent in the size of the sensitization wavelength band ranging from the light region to a near-infrared region, high photosensitivity, stability (endurance), safety, coating and processability, economical efficiency, etc. To phthalocyanines, copper, vanadium, iron, cobalt, nickel, titanium, The various metal phthalocyanines in which a metal ion and complex salt, such as a zirconium, indium, germanium, tin, lead, molybdenum, and silicon, were formed, or the non-metal phthalocyanines which do not contain metal are known, and all are known as useful OPC.

[0005] This invention is concerned with the manufacturing method of the non-metal phthalocyanines in phthalocyanines, . As [indicate /, for example to JP,44-14106,B / especially] The X type non-metal phthalocyanines which performed mechanical processing to the alpha type non-metal phthalocyanines of super-low activity as OPC, and were changed into the crystal form high activity and useful as a photoconductivity material in electrophotography (what is called cross metal free phthalocyanine in this gazette), Or although concerned with the manufacturing method of the non-metal phthalocyanines which cover a near-infrared region from a light region, and show high photosensitivity like a thing (namely, X type non-metal phthalocyanines) of the same

type as cross metal free phthalocyanine given in JP,2-233769,A, For example, it is insufficient just to demonstrate the characteristics (for example, high photosensitivity, a large sensitization region, a small dark decay, etc.) which used and were excellent in an application member like an electro photography photo conductor, and if it seems that a trouble is not collectively caused at the time of this application member manufacture, it cannot be used industrially.

[0006]That is, an application member, for example, an electro photography photo conductor, makes an application layer usually form in up to conductive substrates (not only plate-like but the curved thing is included), such as various kinds of metal, a metal laminate film and paper, the film and paper that were processed by the conducting agent, metal fiber mixed papermaking, and a nonwoven fabric, filmy, and it is manufactured. Although thin film forming of paints like phthalocyanine may be carried out with vacuum deposition at this time, since productivity is remarkably inferior, in now, it has been usually mostly to distribute in an organic solvent with a binder (binder) and other raw materials, and to apply and dry to up to coating liquid, nothing, and a base material.

[0007]Since especially this invention relates to an electro photography photo conductor, describe it in detail, but. If it is also in the structure variously and divides roughly into it, to up to the conductive substrate to which the anchor coat may be given. a photoelectric conversion function like phthalocyanine, although there is a thing of the laminated structure which gave two coats of the thing, and a CGM layer and a coal-tar-mixture layer of the layer structure which distributed and carried out coating of the charge transporting material (coal tar mixture is called) to the remarkable color material (this is called charge generating material CGM) into the insulating binder when necessary, This invention includes X type non-metal phthalocyanines suitable for using for the electro photography photo conductor of all the structures.

[0008]After electrifying electrostatic charge to up to an electro photography photo conductor layer in electrophotography in a dark place, By exposing in the shape of a picture, raise the electrical conductivity of an exposed part and an electric charge is vanished, The latent image which consists of electrostatic charge as a result is made to form, the dry coloring powder or coloring powder suspension subsequently called a toner is contacted, and that which obtains the visible image corresponding to an electrostatic latent image (development) is set into the foundations of an imaging process.

[0009]In order to acquire a good picture, smooth nature with the high application layer surface is required. Therefore, paints like the phthalocyanine in the coating liquid for electro photography photo conductor layer manufacture are pulverized coal with a size of several micrometers or less of a near gestalt as spherically as possible, and must not cause deterioration of crystal growth, condensation, etc. during coating liquid storage. However, the coating liquid which carried out preparation using X type non-metal phthalocyanines according to this invention person's experience, Immediately after preparation, when [when the acidity or alkalinity as coating liquid is good, and the electro photography photo conductor applied and manufactured is also unusual] it is and long-term storage of the coating liquid is carried out also by a case, The unusual rise of the abnormalities in acidity or alkalinity, especially viscosity, condensation of paints, a maldistribution, etc. are seen, This invention came to be produced, as a result of it becoming impossible to use it (in that case, the crystal growth to a needle shape crystal not less than several micrometers in length is observed with an electron microscope in many cases), and

examination of the measure being needed and repeating various experiments.

[0010]Non-metal phthalocyanines are organic colors in which what is called same quality different ** or crystal polymorphism that has various crystal structures is shown, The X type non-metal phthalocyanines which are the things of the crystal structure which shows remarkable high photosensitivity in electro photography, For example, as indicated to above-mentioned JP,44-14106,B, Compound beta type (cheap a low crystal structure) first, and, subsequently crystal transition is carried out to alpha type (the maximum unstable crystal structure) by concentrated sulfuric acid / drainage system reprecipitation processing, It can manufacture by finally transforming alpha type non-metal phthalocyanines to an X type (metastable crystal structure) by the mechanical grinding treatment like ball mill grinding, or other means. And it can be judged by utilizing an X diffraction pattern, an infrared spectrum, etc. which crystal form is taken.

[0011]this invention person compounded beta type non-metal phthalocyanines to reference first, and, subsequently to alpha type, transferred articles to it by sulfuric acid / drainage system reprecipitation processing, and the dry grinding method by a ball mill was adopted as a subsequent mechanical grinding treatment method. From the grinding start time, the grade of the crystal transition from alpha type to an X type sampled the granular material of the required minimum quantity for every predetermined time, and utilized and judged the X diffraction pattern and the infrared spectrum. It combined, preparation of the coating liquid was carried out per each sample, viscosity was measured first, the electro photography photo conductor was created within the day, and the electrophotographic-properties value was measured later. And each coating liquid sealed and was stored in the fixed dark place.

[0012]As a result, although it fully transferred to the X type and electrophotographic properties were also good, the coating liquid after storage thickened and deteriorated remarkably, and experienced that use may already become improper as coating liquid.

[0013]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the manufacturing method of the X type non-metal phthalocyanines which gave the application member like the electro photography photo conductor of the outstanding characteristic, and were excellent in the storage stability of this coating liquid for application member manufacture.

[0014]

[Means for Solving the Problem]In a manufacturing method of X type non-metal phthalocyanines which consist of a technical problem of this invention carrying out crystal form transition of the alpha type non-metal phthalocyanines by ball mill dry grinding processing, It was solved by performing ball mill dry grinding processing [total time which exceeds the twice of time of a time of crystal transition from a time of starting ball mill dry grinding processing of alpha type non-metal phthalocyanines to X type non-metal phthalocyanines reaching saturation]. It has been judged with an X diffraction, an infrared spectrum, etc. whether transition reached saturation.

[0015]In alpha type non-metal phthalocyanines, since a maximum strength peak is observed near $2\theta = 7.6$ degree by an X type on the other hand near bragg angle degree $2\theta = 6.8$ degree in an X diffraction pattern (CuKX line) to X-rays of CuKalpha, respectively, A ratio of such peak intensity serves as an index of a rate of an abundance ratio of alpha type / X type. In an infrared spectrum, several absorption peaks of 700 to

800-cm⁻¹, An index about transition from an arrow tension alpha type to an X type is given by that which is notably different by alpha type and an X type (an absorption peak near 754-cm⁻¹ is specific respectively in alpha type at an X type near 733-cm⁻¹).

Therefore, in this invention, these spectra were mainly utilized and a crystal transition grade to an X type was judged (a numerical value of a peak intensity ratio of these is an index for getting to know whether conversion to an X type from alpha type has already been saturated to the last, and is never a quantitative-analysis value).

[0016]Even if a dry grinding method (especially neat milling without additive admixture) by a ball mill considers cost and time and effort, a converting method from alpha type to an X type has it, as indicated also in the above-mentioned publicly known official reports.

[practical] Although JP,4-4264,A has the statement of planet type ball mill (following, planetary mill, and abbreviation) use, since this is what was the same grinder as the conventional ball mill theoretically, combined rotation and revolution of a pot and aimed at shortening of processing time, it is included in a ball mill by this invention. About atmospheric temperature of the circumference of a ball mill at the time of grinding treatment, it seldom needed to take into consideration in the range of a commonsense life temperature. Because, at the time of grinding operation, by ball mill, especially a planetary mill, temperature up is carried out considerably in itself, and temperature up also of the granular material in a pot is fairly carried out along with it.

[0017]In this way, from a grinding start time, according to time progress, a non-metal-phthalocyanines granular material of the required minimum quantity was sampled (for example, [8 hours or 24 hours (every)]), and a grade of crystal transition from alpha type to an X type was judged with an X diffraction pattern, an infrared spectrum, etc. It combined, preparation of the coating liquid was carried out per each sample, viscosity at 20 ** was promptly measured using E type viscosity meter, an electro photography photo conductor was created within the day, and an electrophotographic-properties value was measured later. And each coating liquid sealed, and was stored in a fixed dark place (<=25 **), viscosity etc. were measured at intervals of one week, and the shape of liquid observed [fitness or] whether it would be poor also by viewing.

[0018]As a result, conversion to an X type from alpha type reaches saturation, and a sample of grinding time which becomes good an electrophotographic-properties value from the first, It turned out that were thickening coating liquid one week afterward, the viscosity rise was increasingly carried out after it, even condensation of a blue pigment and separation (maldistribution) from a vehicle were accepted, and a sample which carried out grinding treatment over time longer than it has also already come to a state which cannot be applied. However, in a sample which carried out grinding treatment for time to exceed the twice of crystal form transition saturation attainment grinding time. Also after the coating liquid stored one week afterward several weeks or more from the first, deterioration of thickening etc. was not accepted and, as for an electro photography photo conductor moreover created using coating liquid after storage, aggravation was not seen at all not only in a spreading surface state but in its electrophotographic properties.

[0019]Although an irrational thing is seemed so to speak, covering a long time in which it is industrially considered to be usually to finish grinding treatment in minimum time judged that conversion to an X type is enough as above-mentioned JP,44-14106,B etc.

see, and it exceeds the twice, and continuing grinding treatment in addition, In this invention, it was found out for the first time that it is a method with a suitable method of

starting to give an X type non-metal-phthalocyanines paints granular material excellent in coating liquid storage stability. As this reason, a mechanochemical decomposition reaction occurs a little, a small amount of impurities generate, and it thinks for it to act on a granular material and to prevent crystal growth.

[0020]

[Example]Next, an example explains this invention still in detail. The part and % which are shown below are a weight reference as long as there is no notice.

[0021]The following operations were performed using the beta type non-metal phthalocyanines which referred to methods (journal OBU heterocyclic chemistry, the 7th volume, 1403 pages, 1970 annual publications), such as example 1P.J. BURACHI, and compounded them as start paints. Under ice water bath cooling, it added to 2,000 copies of special grade chemical sulfuric acid (97% of concentration) gradually, and dissolved in them, and these 100 copies of paints (beta type purple crystal) were filtered using the glass filter. It hung for 30 minutes, it was dropped, keeping this solution at 20 °C or less to the distilled water of 10,000 copies, it settled for a time overnight [after-churning], and suction separation of the post precipitation except supernatant liquor was carried out on the inclination, the filter cake was rinsed until it became neutrality, and also it rinsed repeatedly. After washing with methanol finally, it dried more than a night at 70 °C, and 92 copies of alpha type non-metal phthalocyanines were obtained.

[0022]120 g of the alpha type non-metal phthalocyanines obtained by the above-mentioned method was taken in the pot made from alumina (capacity of 2,000 ml), 2,000 g of balls made from alumina (20 mm in diameter) were put in, and ball mill grinding treatment was started with the revolving speed of 100 revolutions per minute in the thermostatic chamber adjusted in room temperature of 40 °C. After an appropriate time, the required minimum quantity of the paints granular material was sampled to every one day (24 hours) in principle, and the X diffraction pattern and the infrared absorption spectrum were measured. Grinding treatment was performed in 35 days.

[0023]In the non-metal phthalocyanines 0 hour, i.e., grinding, before grinding treatment. In the X diffraction pattern which makes a line source X-rays equivalent to the wavelength of CuKalpha, Degree of bragg angle 2θ =6.80, 7.45, 13.67, 13.85, 14.98, 15.71, 16.18, 20.55, 22.13, 24.27, 26.68, 26.87, 27.05, 27.21, 27.38, 27.50, The strong specific diffraction peak was observed in 27.62 degrees in a ±0.2-degree error span, and it was checked that it is alpha type. In the infrared absorption spectrum, the absorption peak peculiar to three alpha types of 765 (weakness) and 733 (strongest) or 713-cm^{-1} (a little more than) was observed in the 700-cm^{-1} stand. To the sample between eight days of grinding treatment (8x24 hours), very much, In an X diffraction pattern, at degree of bragg angle 2θ =7.60, 9.18, 11.24, 14.38, 15.24, 16.84, 17.37, 20.40, 20.89, 21.66, 22.30, 23.88, 26.25 and 27.36, and 28.63 or 30.56 degrees. The strong specific diffraction peak was observed in the X type in the error span of ±0.2 degrees. However, 2θ = since the weak peak (shoulder) by 6.82 degrees was observed in untransferred alpha type, the ratio of the intensity to 2θ =7.60 degree peak intensity was calculated. Other sampling samples were performed similarly.

[0024]The paints granular material sample extracted day by day [1] in principle carried out preparation of the coating liquid by the following combination, created the electro photography photo conductor, and measured the electrophotographic-properties value. Non-metal-phthalocyanines granular material sample One-copy acrylic copolymer

(binder) Five-copy dioxane (organic solvent) These 3 person with a glass bead 80 copies 2 hours in a well-closed container, By shaking using a paint conditioner, it was made to distribute, the glass bead was removed with the sieve, and the coating liquid of dark blue was obtained. The viscosity at 20 ** was promptly measured using E type viscosity meter. On up to the aluminum plate which carried out surface anodizing of each coating liquid, it applied so that the solid content coverage after desiccation might serve as 5 g/m² using a wire bar, and after desiccation, it put in to **** and put at 80 ** on the 1st. The coating liquid remainder was stored in a dark place 25 ** or less among the well-closed container. [0025]The data about the storage stability of ball mill grinding treatment time and coating liquid is shown in Table 1. Although the viscosity of coating liquid and appearance are normaler irrespective of grinding time on the preparation day than irrespective of Table 1, In the coating liquid which uses the paints granular material on zero to grinding time the 21st, only when abnormalities (thickening, condensation, a maldistribution, etc.) are caused to viscosity and appearance after three to four weeks of storage and grinding treatment is merely performed the 28th day or more, it turns out that the storage stability of coating liquid is good.

[0026]The monolayer type electronic photo conductor created using preparation coating liquid performed electrophotographic-properties measurement with electrostatic recording test equipment (product SPmade from Kawaguchi electrical and electric equipment-428).

Measuring condition: Impressed electromotive force +6 kV, light source A tungsten lamp, sample face illumination of 2 luxs [0027]The intensity ratio and electrophotographic-properties value of each unique peak in the X diffraction pattern for every grinding treatment time are shown in Table 2. As for peak intensity and V₀ (bolt), in Table 2, the surface potential residual percentage for [dark place] 10 seconds, and E_{1/2} (lux and second) of initial potential and DD (%) are [I] potential reduction-by-half light exposures.

[0028]

[Table 1]

摩砕時間と塗液の粘度（20℃）および目視評価結果

摩 砕 時 間 (日数)	調 液 当 日		3 週 間 後		4 週 間 後	
	粘 度 (c p)	目視 評価	粘 度 (c p)	目視 評価	粘 度 (c p)	目視 評価
0日	42.6	○		—		—
1日	28.4	○	53.3	●	58.9	●
2日	30.3	○	45.3	●	43.8	●
3日	25.1	○	49.2	●	52.6	●
4日	21.3	○	58.4	●	64.4	●
5日	22.5	○	87.5	●	93.5	●
6日	25.8	○	63.2	●	68.1	●
7日	26.3	○	71.0	△	73.7	●
8日	26.2	○	121.1	●		●
9日	25.8	○	137.0	●		●
10日	25.3	○	128.7	●		●
11日	26.0	○	105.2	●		●
12日	26.1	○	120.6	●		●
13日	26.4	○	56.6	△	97.5	●
14日	27.1	○	102.1	●		●
21日	26.5	○	107.3	●		●
28日	24.5	○	30.7	○	30.8	○
35日	25.0	○	32.8	○	31.7	○

O expresses fitness among Table 1, ** expresses a defect, and - expresses a defect a little.
[0029]

[Table 2]

摩砕時間とX線回折パターンにおける特異ピークの強度比
および電子写真特性値 (調液直後)

摩 砕 時 間 (日)	X線回折パターン			電子写真特性値		
	$I_{6.8}^{\circ}$ (A)	$I_{7.6}^{\circ}$ (B)	強度比 (A/B)	$V_{0.1}$ (μ lt)	DD (%)	$E_{1/2}$ (1・秒)
0	1535	915	1.68			
1						
2	1260	896	1.41	274	74.0	9.94
3						
4	1190	1040	1.14	285	92.3	5.36
5						
6	564	968	0.58	292	96.9	3.24
7	643	1130	0.57	296	97.0	3.04
8	597	1314	0.45	299	96.8	2.92
9	500	1269	0.39	309	96.1	3.04
10	576	1415	0.41	293	96.2	2.96
11	475	1392	0.34			
12	567	1487	0.38			
13	482	1143	0.42			
14	486	1134	0.43	299	96.6	2.96
21	420	953	0.44	316	97.8	3.04
28	420	1101	0.38	305	97.4	3.00
35	464	1168	0.40	295	96.3	2.84

[0030]Although the intensity ratio ($I_{6.8}^{**}/I_{7.6}^{**}$) of the peak near 2 theta= 6.8 degree of an X diffraction pattern and near 7.6 degree becomes small and goes with time progress from a grinding start from Table 2, it becomes almost fixed after the 9th from the grinding time 8, and it turns out that electrophotographic properties are also fixed-ized. Therefore, it turns out that the grinding time when transition to an X type reaches saturation in this case is for eight to nine days. However, the storage stability of the coating liquid which carried out preparation using the paints granular material for nine days from the grinding time 8 is poor, and coating liquid with good storage stability is obtained only after carrying out grinding treatment for the time of the 28th day or more, as Table 1 shows.

[0031]15g of alpha type non-metal phthalocyanines obtained by the method of the statement in the example 2 Example 1 are taken, putting in to the pot made from agate (capacity of 250 ml) -- seven balls made from agate (20 mm in diameter) -- in addition, using the planetary mill P-5 (made in Fritsch Japan), it was set as disk 360 revolution per minute and pot 780 revolution per minute, and grinding treatment was carried out at the room temperature ($\leq 25^{\circ}$). In principle, with eight time intervals, the paints granular material of the required minimum quantity was sampled, and various measurement was performed like Example 1. Grinding treatment was performed for a maximum of 120 hours.

[0032]Although the viscosity and the visual evaluation result after four weeks of dark place storage of preparation that day and 25 ** or less of the coating liquid which carried out preparation to planetary mill grinding treatment time using each paints granular material sample are shown in Table 3, Although the visual evaluation result of the viscosity of preparation that day is also low good irrespective of the merits and demerits of grinding time, what becomes poor [when it becomes after four weeks of storage, many are carrying out the viscosity rise, and / a visual evaluation result] occurs one after

another. However, only within the coating liquid which carried out preparation using the granular material sample which carried out grinding treatment for 72 hours or more, the state even with after [good] four weeks of storage is held.

[0033]On the other hand, alpha type in FT-infrared spectrum (KBr tablet method) of the granular material sample of each grinding time and the X type were asked for the extinction quotient of two specific absorption peaks. And using each preparation coating liquid, the monolayer type electro photography photo conductor was created like Example 1, and the electrophotographic-properties value was measured by the too same method. A result is summarized in Table 4 and shown.

[0034]

[Table 3]

摩砕時間と塗液の粘度（20℃）および目視評価結果

摩 砕 時 間 (時間)	調 液 当 日		4 週 間 後	
	粘 度 (c p)	目視 評価	粘 度 (c p)	目視 評価
0	42.6	○		—
8	29.5	○	71.7	●
16	29.2	○	95.3	●
24	29.2	○	146.2	●
32	25.3	○	155.5	●
40	26.5	○	170.2	●
48	24.8	○	165.6	●
56	26.0	○	107.0	●
64	27.1	○	51.5	△
72	24.5	○	28.2	○
96	25.7	○	28.9	○
120	26.2	○	32.1	○

O expresses fitness among Table 3, ** expresses a defect, and - expresses a defect a little.

[0035]

[Table 4]

摩砕時間と赤外線スペクトルにおける特異ピークの吸光度比
および電子写真特性値（調液直後）

砕 間 時間	赤外線スペクトルの吸光度			電子写真特性値		
	733 cm ⁻¹ (A)	754 cm ⁻¹ (B)	吸光度比 (A/B)	V ₀ ボルト	DD (%)	E _{1/2} (1・秒)
0	0.123	0	∞			
8	0.067	0.054	1.241	275	71.5	8.06
16	0.087	0.085	1.024	289	91.9	3.56
24	0.183	0.206	0.888	296	96.1	3.24
32	0.360	0.439	0.820	295	96.3	3.04
40						
48	0.772	0.967	0.798	305	96.4	3.24
56						
64						
72	0.319	0.389	0.820	306	97.6	3.16
96	0.357	0.432	0.826	284	97.5	2.96
20	0.508	0.629	0.808	302	96.7	3.00

[0036]Although the extinction quotient (Abs.₇₃₃/Abs.₇₅₄) of the peak near 733-cm⁻¹ of an infrared spectrum and near 754-cm⁻¹ becomes small and goes with grinding lapsed time in Table 4, It becomes almost fixed after grinding time 32 hour, and it also fixed-izes electrophotographic properties. Therefore, it turns out in this case that transition saturation attainment grinding time is 32 hours. However, even if hung from the first still

longer time for grinding time 32 hours, the storage stability of the coating liquid which carried out preparation using those paints granular materials was poor, and coating liquid with good storage stability was obtained only after covering the long time of 72 hours or more and grinding, as Table 3 showed.

[0037]When preparation is carried out in example 3 Examples 1 and 2 and an electro photography photo conductor is created by the method of having indicated, using the coating liquid after four-week storage, from the coating liquid thickened remarkably. Since only the thing of the bad spreading side where leveling of liquid has muscle-like coating unevenness bad was obtained at the time of spreading, measurement of electrophotographic properties was omitted. However, since the thing of the normal spreading side was obtained from coating liquid with good storage stability, the electrophotographic-properties value was measured. A result is shown in Table 5.

[0038]

[Table 5]

貯蔵4週間後塗液塗布サンプルの電子写真特性値

摩 砕 方 法	摩 砕 時 間	電 子 写 真 特 性 値		
		V ₀ (ボルト)	DD (%)	E _{1/2} (1・秒)
ボール ミル	28日間	297	97.5	3.02
	35日間	304	97.9	2.76
遊 星 ミル	72時間	309	96.1	3.04
	96時間	295	96.3	3.24
	120時間	305	96.4	3.16

[0039]From Table 5, even if it compares the electrophotographic-properties value of the application member created from coating liquid (after four weeks of storage) with good storage stability with the value of the application member created immediately after preparation, degradation is not accepted but is understood that storage stability is good also in electrophotographic properties.

[0040]

[Effect of the Invention]In the manufacturing method of the X type non-metal phthalocyanines by the ball mill dry grinding of alpha type non-metal phthalocyanines, If it grinds [the total time which starts dry grinding and exceeds the twice of time until the crystal transition to X type non-metal phthalocyanines is enough to reach saturation], The X type non-metal phthalocyanines which were excellent in the characteristic when it was used for the application member like an electro photography photo conductor, and were excellent in the storage stability of this coating liquid for application member manufacture can be manufactured. And the advance grade of crystal transition can be judged by utilizing the measuring means of an X diffraction pattern, an infrared spectrum, etc.

Claim(s)]

[Claim 1]In a manufacturing method of X type non-metal phthalocyanines which consist of carrying out crystal form transition of the alpha type non-metal phthalocyanines by ball mill dry grinding processing, A manufacturing method of X type non-metal

phthalocyanines performing ball mill dry grinding processing [total time which exceeds the twice of time of a time of crystal transition from a time of starting ball mill dry grinding processing of alpha type non-metal phthalocyanines to X type non-metal phthalocyanines reaching saturation].